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54 CLAY FILLED POLYPHENYLENE ETHER COMPOSITIONS.

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FR-A-2 376 185
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US-A-3 708 455
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US-A-4 166 812
US-A-4 233 199
US-A-4 239 673 | |

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Description

This invention relates to clay filled polyphenylene ether compositions, and more specifically, to compositions composed of polyphenylene ether, an impact modifier and a plasticizer which also contain clay particles characterized by a certain specified particle size and surface area.

Background of the invention

The polyphenylene ether resins are well known in the art as comprising a family of thermoplastic materials which are suitable for various engineering purposes. These may be made by catalyzed and non-catalyzed processes described in the patent literature, such as in Hay, U.S. 3,306,874 and 3,306,875, and in Stamatoff, U.S. 3,257,357 and U.S. 3,257,358.

It is known that the polyphenylene ether resins may be admixed with polystyrene, either unmodified or modified, to produce compositions having properties better than those of either of the two polymers individually. Such compositions are disclosed in Cizek, U.S. 3,383,435.

To reduce the cost, it has been proposed to add mineral fillers such as aluminum silicate, calcium carbonate, magnesium silicate, calcium silicate, silica or others, to compositions containing a polyphenylene ether resin and polystyrene. Compositions comprising a polyphenylene ether resin, a rubber modified high-impact polystyrene and aluminum silicate are disclosed in U.S. 4,166,812.

It is known that the addition of mineral fillers to polyphenylene ether resins can increase the rigidity and dimensional stability of the polymers. The toughness of the resulting composite is usually lower than that of the mineral filled-free polymer, however. It has been found that some mineral fillers increase the rigidity of the polymer and provide ductile composites having good impact resistance. Such benefits are more pronounced in falling weight-type impact tests, such as Gardner impact resistance. This type of impact resistance is much more important in actual practice than the impact resistance as measured by other means such as the Izod impact test.

It has now been discovered that as among mineral fillers in general, particulate clay and specifically clay having a mean particle size of less than 0.6 micrometer and a surface area of 15 square meters per gram (m^2/g) or more, dramatically improves the Gardner impact strength of certain polyphenylene ether compositions. These compositions are described below.

Description of the invention

According to this invention, there are provided thermoplastic compositions having improved impact strength when molded, comprising:

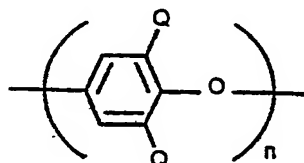
- (a) a polyphenylene ether resin, alone, or together with an impact modifier;
- (b) an effective amount of a plasticizer; and
- (c) a particulate clay filler having a mean

particle size of less than 0.6 micrometer and a surface area of at least 15 square meters per gram.

Preferably, the particulate clay filler is substantially free of large, gritty particles and has been well dispersed to avoid the formation of lumps. The presence of grit and clumps may cause stress concentrations in the clay-resin composites which lower the impact resistance and also other physical properties.

The clay filler of the compositions of this invention can be prepared by conventional methods, using, e.g., sieving means to separate and collect clay particles having the appropriate size, preferably 0.1 to 0.6 micrometer, and surface area, preferably 15 to 30 m^2/g , and to separate gritty and surface particles and clumps.

The preferred polyphenylene ether resins are those having the formula:



wherein the oxygen ether atom of one unit is connected to the benzene nucleus of the next adjoining unit, n is a positive integer and is at least 50, and each Q is a monovalent substituent selected from the group consisting of hydrogen, halogen, hydrocarbon radicals free of a tertiary alpha-carbon atom, halohydrocarbon radicals having at least two carbon atoms between the halogen atom and the phenyl nucleus, hydrocarbonoxy radicals and halohydrocarbonoxy radicals having at least two carbon atoms between the halogen atom and the phenyl nucleus.

The preparation of polyphenylene ether resins corresponding to the above formula is described in the above-mentioned patents of Hay and Stamatoff.

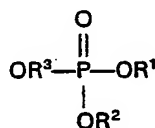
The most preferred polyphenylene ether resin for use in this invention is poly(2,6 - dimethyl - 1,4 - phenylene)ether.

The particular impact modifier employed in the compositions is not critical and can be selected from a wide variety of elastomeric materials. By way of illustration, the term "impact modifier" employed herein includes copolymers of styrene and elastomeric materials such as acrylonitrile, EPDM rubber, maleic anhydride or diene rubber. Examples include copolymers of styrene and acrylonitrile, copolymers of styrene and butadiene, copolymers of styrene and maleic anhydride and copolymers of styrene and EPDM rubber. Other examples include terpolymers of styrene, acrylonitrile and butadiene, and terpolymers of styrene, butadiene and styrene of the A-B-A type or radial teleblock type, either hydrogenated or unhydrogenated.

Special mention is made of the A-B-A¹ block copolymers wherein terminal blocks A and A¹ are

the same or different and are derived from a vinyl aromatic compound, e.g., styrene, α -methyl styrene, vinyl toluene, vinyl xylene, vinyl naphthalene, and the like, and center block B is derived from a conjugated diene, i.e., butadiene, isoprene, 1,3-pentadiene, 2,3-dimethyl butadiene, and the like. Hydrogenated derivatives of the foregoing are also preferred. Both the unhydrogenated and hydrogenated forms can be prepared by methods described in the patent literature, e.g., U.S. 3,251,905; U.S. 3,231,635; and U.S. 3,431,323.

The plasticizer can be selected from among any materials known to impart compatibility with polyphenylene ether resin. Preferably, the plasticizer is an aromatic phosphate, and especially a compound having the formula:



wherein R^1 , R^2 and R^3 are the same or different and are alkyl, haloalkyl, cycloalkyl, halocycloalkyl, aryl, haloaryl, alkyl substituted aryl, haloalkyl substituted aryl, aryl substituted alkyl, haloaryl substituted alkyl, hydroxyalkyl, hydroxyaryl, hydroxyalkaryl, halogen and hydrogen.

Examples include cresyl diphenyl phosphate, 2-ethylhexyl diphenyl phosphate, tricresyl phosphate, triisopropylphenyl phosphate, triphenyl phosphate, triethyl phosphate, dibutyl phenyl phosphate, diethyl phosphate, cresyl diphenyl phosphate, isooctyl diphenyl phosphate, tributyl phosphate, 2-ethylhexyl diphenyl phosphate, isodecyl diphenyl phosphate, isodecyl dicresyl phosphate, didecyl cresyl phosphate, tri-*n*-hexyl phosphate, di-*n*-octyl phenyl phosphate, di-2-ethylhexyl phenyl and tri-2-ethylhexyl phosphate or

mixtures thereof. Especially preferred is triphenyl phosphate.

The ingredients in the compositions of this invention can vary widely. In preferred embodiments, the compositions contain from 5 to 95 parts by weight of polyphenylene ether, from 95 to 5 parts by weight of impact modifier, from 5 to 50 parts by weight of plasticizer and from 5 to 50 parts by weight of clay.

Other ingredients, such as stabilizers, flame retardant agents, drip retardants, antioxidants, antistatic agents, coloring agents, pigments, mold release agents, and the like, can also be included for their conventionally employed purposes.

The compositions of this invention are prepared in any manner. Usually, however, the ingredients are formed into a preblend by tumbling in a mixer, the preblend is extruded at a temperature of from 288°C (550°F) to 327°C (620°F), the extrudate is cut into smaller pieces, and the pieces are injection molded at a temperature of from 277°C (530°F) to 338°C (640°F).

Description of the preferred embodiments

The compositions of this invention are illustrated in the following examples, which are not intended to be limiting.

Examples 1—14

Compositions according to this invention are prepared by tumbling the ingredients, extruding the resulting blend in a Werner Pfleiderer 28 mm twin screw machine, at a temperature of 310°C (590°F) and injection molding the extrudate in a Newbury injection molding machine at 316°C (600°F) (mold temperature 82°C (180°F)).

The molded compositions are evaluated for physical properties according to ASTM standards. The compositions and properties are reported in Tables I and II.

TABLE I
Compositions comprising a polyphenylene ether resin, an A-B-A block copolymer, triphenyl phosphate and clay filler

Ingredients, parts by weight	1	2*	3*	4*	5*	6*	7*
Poly(2,6-dimethyl-1,4-phenylene)ether	95	95	95	95	95	95	95
Hydrogenated styrene-butadiene-styrene copolymer ^a	5	5	5	5	5	5	5
Triphenyl phosphate	10	10	10	10	10	10	10
ASP-100® ^b (clay)	25	—	—	—	—	—	—
ASP105® ^b (clay)	—	25	—	—	—	—	—
ASP-170® ^b (clay)	—	—	25	—	—	—	—
ASP-900® ^b (clay)	—	—	—	25	—	—	—
ASP-400® ^b (clay)	—	—	—	—	25	—	—
Satintone 4® ^b (clay)	—	—	—	—	—	25	—
Satintone 1® ^b (clay)	—	—	—	—	—	—	25

^a Shell Chemical Company's Kraton G 1652® ^b Engelhard Minerals & Chemicals Corporation * comparison experiment

TABLE I. (cont'd)
Sample designations

Physical properties	1	2*	3*	4*	5*	6*	7*
Filler	ASP-100®	ASP-105®	ASP-170®	ASP-900®	ASP-400®	Satintone® No. 4	Satintone® No. 1
Mean particle size of filler (μm)	0.55	0.55	0.55	1.5	4.8	1.0	20
Surface area of filler (m ² /g)	14.6—16.2	11.1—13.8	11.5—14.3	11	7.2	8.9—9.5	7.3—8.5
Gardner impact strength of composite N.m (in-lbs)	26.55 (235)	7.12 (63)	3.05 (27)	1.01 (9)	0.225 (2)	1.41 (12.5)	0.73 (6.5)

TABLE II
Compositions comprising a polyphenylene ether resin, an A-B-A block copolymer, triphenyl phosphate and clay filler

Ingredients, parts by weight	8	9	10	11	12*	13*	14*
Poly(2,6-dimethyl-1,4-phenylene)ether	95	95	95	95	95	95	95
Hydrogenated styrene-butadiene-styrene copolymer ^a	5	5	5	5	5	5	5
Triphenyl phosphate	10	10	10	10	10	10	10
HG-90® ^b (clay)	25	—	—	—	—	—	—
Suprex® ^b (clay)	—	25	—	—	—	—	—
Nulok 321® ^b (clay)	—	—	25	—	—	—	—
Nucap 200® ^b (clay)	—	—	—	25	—	—	—
Al-Sil-Ate NCF® ^c (clay)	—	—	—	—	25	—	—
Al-Sil-Ate NC® ^c (clay)	—	—	—	—	—	25	—
Al-Sil-Ate HO ₂ ® ^c (clay)	—	—	—	—	—	—	25

* comparison experiment ^a Shell Chemical Company's KRATON G 1652 ^b J. M. Huber Corporation ^c Freeport Kaolin Company

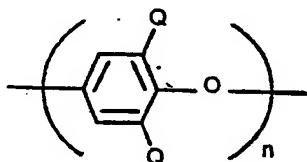
TABLE II (cont'd)
Sample designations

Physical properties	8	9	10	11	12*	13*	14*
Filler	HG-90	Suprex	Nulok No. 321	Nucap No. 200	Al-Sil-Ate NCF	Al-Sil-Ate NC	Al-Sil-Ate NO ₂
Mean particle size of filler (μm)	0.3	0.3	0.3	0.3	97% below 2	82% below 2	82% below 2
Surface area of filler (m ² /g)	22	22	22	22	14—16	12—14	12—14
Gardner impact strength of composite N · m (in-lbs)	25.42 (225)	25.42 (225)	21.47 (190)	23.72 (210)	10.73 (95)	1.69 (15)	1.69 (15)

It can be seen that the compositions according to the invention, 1, 8, 9, 10 and 11, each containing clay having a mean particle size no greater than 0.6 micrometer and a surface area of at least 15 m²/g, provide clearly better Gardner impact strength in comparison with the compositions containing a clay filler not in accordance with the invention, 2—7 inclusive and 12—14 inclusive.

Claims

1. A thermoplastic composition comprising:
 - (a) a polyphenylene ether resin, alone, or together with an impact modifier;
 - (b) an effective amount of a plasticizer; and
 - (c) a particulate clay filler having a mean particle size of less than 0.6 micrometer and a surface area of at least 15 square meters per gram.
2. A composition as defined in Claim 1, in which the impact modifier is an A-B-A¹ block copolymer wherein terminal blocks A and A¹ are derived from a vinyl aromatic compound and center block B is derived from a conjugated diene.
3. A composition as defined in Claim 2, in which the terminal blocks are polystyrene and the center block is polybutadiene.
4. A composition as defined in Claim 2, in which the A-B-A¹ block copolymer has been hydrogenated.
5. A composition as defined in Claim 1, in which the polyphenylene ether resin has the formula



wherein the oxygen ether atom of one unit is connected to the benzene nucleus of the next adjoining unit, n is a positive integer and is at least 50, and each Q is a monovalent substituent selected from the group consisting of hydrogen, halogen, hydrocarbon radicals free of a tertiary alpha-carbon atom, halohydrocarbon radicals having at least two carbon atoms between the halogen atom and the phenyl nucleus, hydrocarbonoxy radicals and halohydrocarbonoxy radicals having at least two carbon atoms between the halogen atom and the phenyl nucleus.

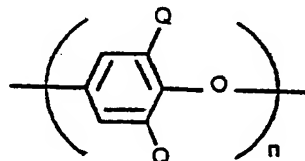
6. A composition as defined in Claim 1, in which the polyphenylene ether resin is poly(2,6-dimethyl-1,4-phenylene)ether.
7. A composition as defined in Claim 1, in which the plasticizer is triaryl phosphate.
8. A composition as defined in Claim 1, in which the plasticizer is triphenyl phosphate.
9. A composition as defined in Claim 1, comprising from about 5 to about 95 parts by weight of said polyphenylene ether resin, from about 95 to 5 parts by weight of said impact modifier, from

about 5 to about 50 parts by weight of said plasticizer and from about 5 to about 50 parts by weight of said clay.

10. A composition as defined in Claim 1, in which the particulate clay filler has a mean particle size of from 0.1 to 0.6 micrometer and a surface area of from 15 to 30 square meters per gram.

Patentansprüche

1. Thermoplastische Zusammensetzung enthaltend:
 - (a) ein Polyphenylenätherharz allein oder zusammen mit einem Schlagmodifizierungsmittel,
 - (b) eine wirksame Menge eines Weichmachers und
 - (c) einen teilchenförmigen Tonfüllstoff mit einer mittleren Teilchengröße von weniger als 0,6 Mikrometer und einer Oberflächenzone von wenigstens 15 m²/g.
2. Zusammensetzung nach Anspruch 1, in der das Schlagmodifizierungsmittel ein A-B-A¹ Blockcopolymer ist, worin die Endblöcke A und A¹ von einer vinylaromatischen Verbindung abgeleitet sind und der Zentralblock B von einem konjugierten Dien abgeleitet ist.
3. Zusammensetzung nach Anspruch 2, in der die Endblöcke Polystyrol und der Zentralblock Polybutadien ist.
4. Zusammensetzung nach Anspruch 2, in der das A-B-A¹-Blockcopolymer hydriert worden ist.
5. Zusammensetzung nach Anspruch 1, in der das Polyphenylenätherharz die Formel



aufweist, worin das Äthersauerstoffatom einer Einheit mit dem Benzolkern der nächsten benachbarten Einheit verbunden ist, n eine positive ganze Zahl ist und wenigstens 50 beträgt und jedes Q ein einwertiger Substituent ausgewählt aus der Gruppe bestehend aus Wasserstoff, Halogen, Kohlenwasserstoffresten, die frei sind von einem tert. α-Kohlenstoffatom, halogenierten Kohlenwasserstoffresten mit wenigstens zwei Kohlenstoffatomen zwischen dem Halogenatom und dem Phenylkern, Kohlenwasserstoffoxyresten und Halogenkohlenwasserstoffoxyresten mit wenigstens zwei Kohlenstoffatomen zwischen dem Halogenatom und dem Phenylkern ist.

6. Zusammensetzung nach Anspruch 1, in welcher das Polyphenylenätherharz Poly(2,6-dimethyl-1,4-phenylen)-äther ist.

7. Zusammensetzung nach Anspruch 1, in welcher der Weichmacher Triarylphosphat ist.

8. Zusammensetzung nach Anspruch 1, in welcher der Weichmacher Triphenylphosphat ist.

9. Zusammensetzung nach Anspruch 1, enthaltend etwa 5 bis etwa 95 Gew.-Teile des Polyphenylenätherharzes, etwa 95 bis 5 Gew.-Teile des Schlagmodifizierungsmittels, etwa 5 bis etwa 50 Gew.-Teile des Weichmachers und etwa 5 bis etwa 50 Gew.-Teile des Tons.

10. Zusammensetzung nach Anspruch 1, in welcher der teilchenförmige Ton-Füllstoff eine mittlere Teilchengröße von 0,1 bis 0,6 Mikrometer und eine Oberflächenzone von 15 bis 30 m²/g aufweist.

Revendications

1. Composition thermoplastique comprenant:
(a) une résine de poly(oxyphénylène), seule ou en combinaison avec un agent de modification de la résistance aux chocs.

(b) une quantité efficace d'un plastifiant; et

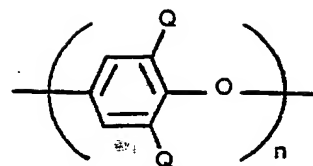
(c) une charge d'argile particulaire présentant une dimension particulaire moyenne inférieure à 0,6 micromètre et une surface spécifique d'au moins 15 mètres carrés par gramme.

2. Composition selon la revendication 1, caractérisée en ce que l'agent de modification de la résistance aux chocs est un copolymère séquencé A-B-A' dans lequel les séquences terminales A et A' sont dérivées d'un composé vinylaromatique et la séquence centrale B est dérivée d'un diène conjugué.

3. Composition selon la revendication 2, caractérisée en ce que les séquences terminales sont des séquences polystyrène et la séquence centrale, une séquence polybutadiène.

4. Composition selon la revendication 2, caractérisée en ce que le copolymère séquencé A-B-B' a été hydrogéné.

5. Composition selon la revendication 1, caractérisée en ce que la résine de poly(oxyphénylène) répond à la formule:



dans laquelle l'atome d'oxygène du groupe éther oxyde d'un motif est relié au nouveau benzène du motif adjacent, n représente un nombre entier positif au moins égal à 50, et chacun des groupes Q représente un substituant monovalent choisi dans le groupe constitué par l'hydrogène, les halogènes, des radicaux hydrocarbonés dépourvus d'atome de carbone tertiaire en α, des radicaux hydrocarbonés halogénés ayant au moins 2 atomes de carbone entre l'atome d'halogène et le noyau phényle, des radicaux oxyhydrocarbonés et des radicaux oxyhydrocarbonés halogénés ayant au moins deux atomes de carbone entre l'atome d'halogène et le noyau phényle.

6. Composition selon la revendication 1, caractérisée en ce que la résine de poly(oxyphénylène) est le poly(oxydiméthyl-2,6-phénylène-1,4).

7. Composition selon la revendication 1, caractérisée en ce que le plastifiant est le phosphate de triaryle.

8. Composition selon la revendication 1, caractérisée en ce que le plastifiant est le phosphate de triphényle.

9. Composition selon la revendication 1, caractérisée en ce qu'elle comprend d'environ 5 à 95 parties en poids de la résine de poly(oxyphénylène), d'environ 95 à 5 parties en poids de l'agent de modification de la résistance aux chocs, d'environ 5 à 50 parties en poids du plastifiant et d'environ 5 à 50 parties en poids de l'argile.

10. Composition selon la revendication 1, caractérisée en ce que la charge d'argile particulaire présente une dimension particulaire moyenne comprise entre 0,1 et 0,6 micromètre et une surface spécifique comprise entre 15 et 30 mètres carrés par gramme.

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